

DEPARTMENT OF COMMERCE AND LABOR

TECHNOLOGIC PAPERS

OF THE

BUREAU OF STANDARDS

S. W. STRATTON, DIRECTOR

No. 8

A RAPID METHOD FOR THE DETERMINATION OF
VANADIUM IN STEELS, ORES, ETC., BASED ON
ITS QUANTITATIVE INCLUSION BY THE
PHOSPHOMOLYBDATE PRECIPITATE

BY

J. R. CAIN, Associate Chemist

and

J. C. HOSTETTER, Assistant Chemist

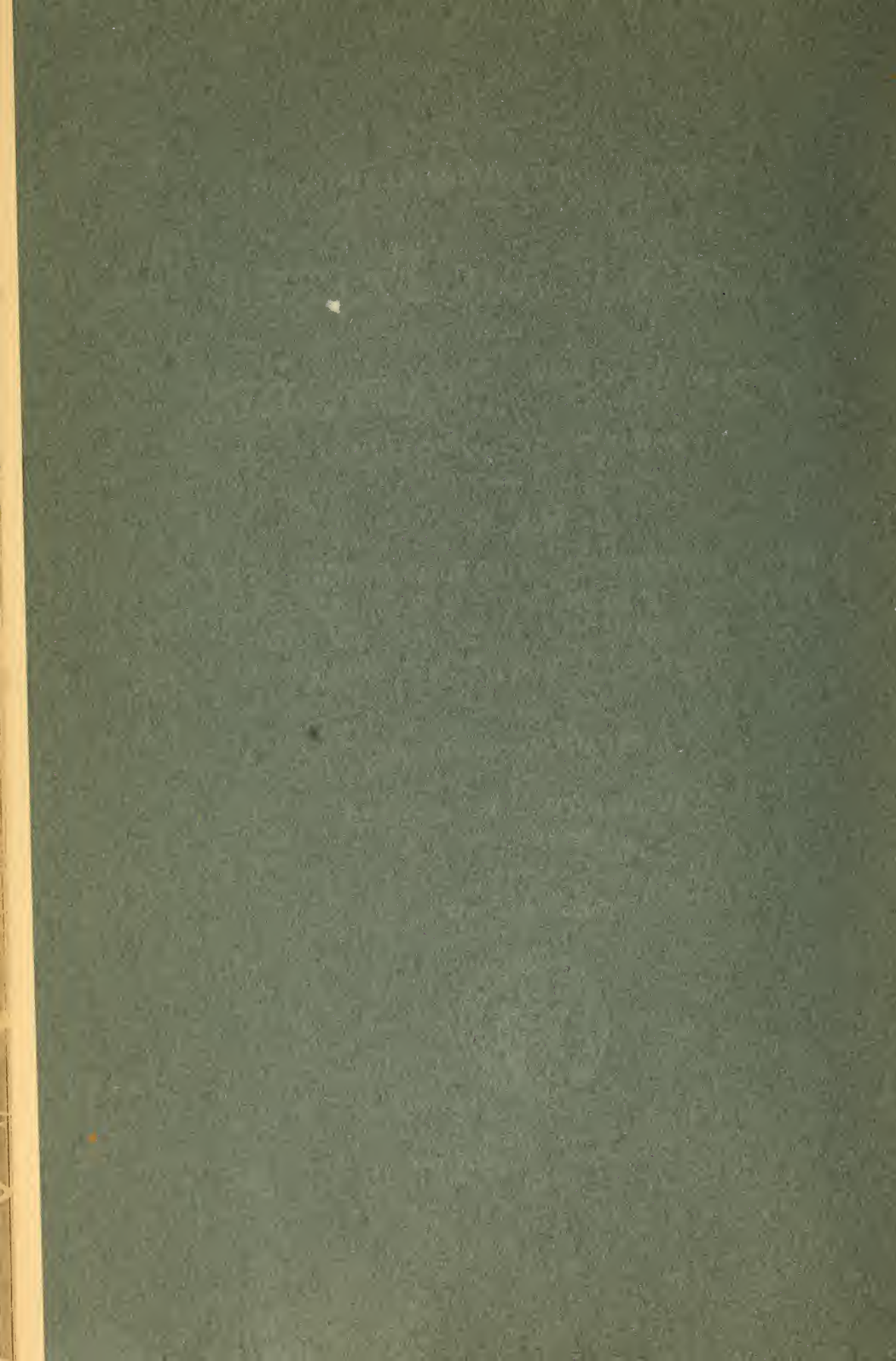
Bureau of Standards

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By J. R. Cain and J. C. Hostetter

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1. INTRODUCTION

The fact that vanadium is carried down with ammonium phosphomolybdate when the latter is precipitated in solutions of the former has long been known. Likewise, the fact that the precipitate so obtained has different properties from the normal phosphomolybdate has been mentioned by several authors. The orange to brick-red color of this vanadium-bearing precipitate is quite different from the color of the normal ammonium phosphomolybdate—called from its color the “yellow precipitate.” Brearley and Ibbotson ¹ mention the increased solubility in dilute nitric acid of the vanadium-bearing precipitate over the normal precipitate and give some conditions to lessen precipitation of vanadium with phosphorus in steel analysis. The phenomenon has usually been studied with regard to the determination of

¹The Analysis of Steel-Works Materials, 1902, p. 165.

phosphorus in the presence of vanadium, since the precipitation of vanadium with ammonium phosphomolybdate interferes with an exact determination of phosphorus by the ordinary methods. Especially is this true in steel analysis. The possibility of easily separating vanadium from iron by this method has, we believe, never before been studied. The present research was undertaken in order to decide whether or not vanadium could be completely precipitated with phosphoric acid; and, if so, to learn if it could be determined quantitatively.

2. PRELIMINARY CONDITIONS FOR PRECIPITATING THE VANADIUM

The necessary ratio of phosphoric acid to vanadic acid for complete precipitation of the latter was investigated qualitatively by following the change in color of the phosphomolybdate precipitated with increasing additions of phosphoric acid. A nitric acid solution of a vanadium-free steel was prepared; to this was added a known amount of vanadium from a carefully standardized ammonium vanadate solution. To equal volumes of the steel solution so prepared were added gradually increasing volumes of a roughly standardized sodium phosphate solution, and the phosphoric acid was precipitated by the molybdate reagent, observing the conditions for this precipitation usually given in texts on steel analysis. With small amounts of phosphoric acid the precipitate was of a deep orange color, which became progressively lighter as the phosphorus increased, finally approaching the color of the normal or vanadium-free phosphomolybdate when relatively very large amounts of phosphoric acid were added. The filtrates were treated by precipitating a further small amount of phosphoric acid, and judging by the color of the precipitate whether or not precipitation was complete the first time. The color of the precipitate proved to be a very delicate qualitative criterion, and very soon it was possible in this manner to fix with fair accuracy the ratio of phosphoric acid to vanadic acid in order to carry down all the vanadium with one precipitation. As methods for the quantitative determination of the vanadium were developed, this ratio

was determined with greater accuracy. The mechanism of the precipitation and the question of this ratio are subjects that will be described in more detail in another paper. It is sufficient for the present purpose to say there is a coprecipitation of vanadium under the above general conditions, which can be accurately enough controlled to make the precipitation uniformly quantitative.

Other questions affecting the probable accuracy of the determination were (1) solubility of the vanadium-bearing precipitate in the usual washing solutions, and (2) the optimum temperature for precipitation. As to the solubility of the precipitate, it was soon found that the presence of vanadium caused marked changes in the solubility of ammonium phosphomolybdate. It was noticed that when the precipitate dissolved to any extent in the washing solutions, these were strongly colored, usually having a straw or orange tint. It was thus possible to decide the question qualitatively, and Table I gives some of the results obtained. It will be seen that acid ammonium sulphate and ammonium nitrate solutions are best adapted for washing the yellow precipitate. Incidentally, the marked solubility in dilute solutions of potassium nitrate and of nitric acid is of interest, for these are the wash solutions recommended by some authorities for use when determining phosphorus in steel. It is evident that such use may occasion errors in the phosphorus determination if vanadium is present in appreciable amount. It seems probable that the solubilities vary considerably with the proportion of vanadium present in the precipitates.

TABLE I

Order of Solubility of Vanadium-Bearing Precipitate² in Various Solvents at Room Temperature

Solvent	Concentration	Color of solution
	Per cent	
Ammonium acid sulphate.....	(3)	Colorless.
Ammonium nitrate.....	(4)	Do.
Do.....	10	Do.
Ammonium sulphate.....	50	Faint yellow.
Nitric acid.....	50	Color increases regularly down the series, showing increasing solubility.
Do.....	25	
Ammonium sulphate.....	30	
Ammonium nitrate.....	1	
Ammonium chloride.....	1	
Ammonium sulphate.....	10	Deep yellow (complete solution).
Sulphuric acid.....	50	
Water.....		
Ammonium molybdate (neut.).....	1	
Potassium nitrate.....	1	
Potassium sulphate ⁵	1	Deep yellow (complete solution).
Nitric acid ⁵	1	
Sodium sulphate ⁵	1	
Ammonium molybdate (neut.) ⁵	10	

² Containing approximately four-tenths of 1 per cent vanadium.

³ See p. 15.

⁴ Saturated solution.

⁵ Five-tenths gram of precipitate dissolves in less than 20 cc of the solvent.

The optimum temperature for precipitation in this connection is governed largely by considerations affecting the physical properties of the precipitate and the speed of precipitation. Accordingly, our precipitations are made from solutions brought to boiling before addition of the precipitant, thus securing a rapidly settling precipitate, readily filtered by suction. Certain reasons, to be considered at another time, would seem to demand a precipitation at this high temperature. Brearley and Ibbotson⁶ also have shown that more vanadium is precipitated at high than at low temperatures.

After having assured ourselves qualitatively that vanadium is completely precipitated by the phosphomolybdate precipitate

⁶ The Analysis of Steel-Works Materials, 1902.

obtained under proper conditions, a study was made of methods for determining the vanadium thus precipitated.

3. SEPARATION OF THE VANADIC ACID FROM THE MOLYBDIC ACID

In view of the easy volatility of molybdic acid, it was at first thought practicable to heat the precipitate over a blast lamp until all the molybdenum had been driven off. It was found that nearly all the molybdenum could be volatilized, but there are too many difficulties encountered to make the method reliable. There is much danger of mechanical loss where the relative amount of vanadium is small; moreover, at the temperature required for rapid volatilization, the vanadium pentoxide remaining behind fuses and creeps over the side of the boat or crucible used as a container, a fact previously noted by Gibbs.⁷ Further, there is usually a slight reduction of molybdenum to a lower oxide which does not volatilize readily. However, this method of handling the precipitate has some merits, particularly if one wants visual confirmation of the presence of vanadium in a sample of material. The characteristic appearance of fused vanadium pentoxide is easily distinguished in the residue after ignition, even though some of the lower (blue) oxide of molybdenum is present. Of course this precipitate can be taken up by fusion with sodium carbonate and precipitated by mercurous nitrate or in any other manner desired. Usually it is accompanied by some iron oxide. We consider that the method is subject to too many irregularities and is too difficult of manipulation for technical work. Moreover, it is much slower than other procedures to be described later. We find that Truchot⁸ had also proposed and made use of the volatility of molybdic acid to separate it from small amounts of vanadium coprecipitated with molybdenum, when electrolyzing ammoniacal solutions of molybdates and vanadates.

A very much simpler and shorter method has been devised by us for separating the vanadium in pure form from the phosphomolybdate precipitate. The latter is suspended in a small amount of hot water, and dilute ammonia added drop by drop, with vigorous

⁷ *Am. Chem. J.*, 5, p. 371; 1883-84.

⁸ *Ann. Chim. Anal.*, 7, pp. 165-167; 1902.

shaking, until everything is in solution. The solution is heated until all but a trace of ammonia is expelled. The success of the operation depends on the presence of a very small amount of free ammonia at this stage. If too much is present, the precipitate subsequently obtained on adding mercurous solution carries down some molybdenum. On the other hand, enough ammonia must be present to form a sufficient volume of amido precipitate to bring down the vanadium. One or two trials will enable the operator to decide as to the proper excess. When the right amount of ammonia is present, the solution is filtered, if necessary, and enough mercurous nitrate solution is added to it to give an appreciable acid reaction with litmus paper.⁹ Usually a voluminous black precipitate separates on shaking; if it does not form and settle rapidly, the solution is heated until it does. The precipitate is washed by decantation two or three times with water containing 1 per cent mercurous nitrate, and is finally transferred to the filter and washed there two or three times more. Filter and contents are transferred to a porcelain crucible, the filter paper burned off, and the mercury volatilized. The vanadium remains partly as vanadic pentoxide, partly as lower oxides and is accompanied by relatively very little molybdenum. The latter may be precipitated, if desired, by hydrogen sulphide (after the vanadium has been dissolved out of the crucible with concentrated sulphuric acid and the solution diluted) leaving a pure vanadium solution. If the vanadium pentoxide is dissolved out of the crucible with concentrated sulphuric acid, the intense brown or orange color, characterizing such solutions of vanadium pentoxide is very marked; if blue or green tints (due to lower oxides of molybdenum and vanadium) are present, these disappear on the addition of a trace of nitric acid, and evaporation until dense fumes appear.

We have not used this method for obtaining quantitative separations of vanadium, although it would probably be successful if the filtrates were treated a second or third time and the precipitates combined. However, by far the greater portion of the vanadium is obtained at first.

⁹ Caused by the hydrolysis of the mercurous nitrate solution.

The principal use we have made of these methods, as stated above, has been for the purpose of actually isolating the vanadium where there could be the slightest doubt as to its being present at all. In this manner, we believe, the value of the method, from a purely scientific standpoint, is increased. For technical or practical purposes it is never necessary to separate the vanadium from the molybdic and phosphoric acids in order to determine it accurately.

4. REDUCTION OF THE VANADIC ACID BY SULPHUR DIOXIDE

Edgar's¹⁰ method of reduction by sulphur dioxide was next tried, with the idea of reducing the vanadium to the tetravalent stage without affecting the molybdenum; the tetravalent vanadium could then be titrated against permanganate, as usual. Edgar found that by properly adjusting the acidity (sulphuric acid) of his solution, and its molybdenum concentration, the differential reduction could be made with ease. Our results are confirmatory, but unfortunately the method is limited in its application to the present problem because of the effect of the presence of iron occluded by the large amount of ammonium phosphomolybdate sometimes required. This iron is sometimes present in relatively large quantities and of course is wholly or in part reduced by the sulphur dioxide. It is difficult, too, to completely eliminate this impurity from the precipitate without unduly prolonging the process. Solution of the precipitate, followed by reprecipitation, helps but little. If the precipitate is dissolved in ammonia, a clear solution is obtained, even if considerable iron is present; the latter reveals its presence by imparting a dark color to the otherwise colorless solution. If, however, the precipitate is dissolved in sodium hydroxide, a large proportion of the iron separates and the precipitation can be made nearly complete by boiling the solution until all the ammonia of constitution of the yellow precipitate is expelled.

¹⁰ Am. J. Sci., 4th series, 25, pp. 332-334, 1908. (See also Gibbs, loc. cit.)

We made a number of fairly accurate determinations of vanadium in the presence of iron and chromium by precipitating the vanadium with phosphomolybdate, dissolving the precipitate in ammonia, acidifying with sulphuric acid to a 15 per cent acidity, followed by sulphur dioxide reduction and permanganate titration. In most of the determinations it was necessary to get rid of the iron contaminating the phosphomolybdate by dissolving the latter in sodium hydroxide solution and filtering off the ferric hydroxide, as above. It was found that chromium in the trivalent condition did not affect the determination of vanadium at all.

A series of determinations by this method now gave the necessary data for accurately fixing the ratio of phosphorus to vanadium to secure complete precipitation. It was established that 10 times as much phosphorus as there is vanadium to be determined would insure complete precipitation of all the vanadium and allow a sufficient margin of safety for variation from suspected composition. We have used this ratio in all subsequent determinations. Of course, where the vanadium content of a sample is not known within sufficiently close limits, it is necessary to make two or more phosphomolybdate precipitations, testing each for vanadium. However, this is about what one has to do with any method when working on unknown materials.

The method of reducing the vanadium by sulphur dioxide and titrating against permanganate having proved, in our opinion, too long and uncertain for technical use, other methods were tried.

5. COLORIMETRIC DETERMINATION OF THE VANADIC ACID

Gregory's colorimetric method,¹¹ depending on the colors developed in strong sulphuric-acid solutions of vanadium and strychnine, seemed promising, inasmuch as the phosphomolybdate is so soluble in concentrated sulphuric acid. We found by preliminary tests that the associated molybdenum has no appreciable effect on the strychnine, so far as color development is concerned. However, iron does, and this is to be expected from Allen's state-

¹¹ Chem. News, 100, p. 221; 1909.

ment of the cause of the color:¹² "On treating a cold solution of strychnine in concentrated sulphuric acid with an oxidizing agent of almost any kind a rich purple-blue coloration is developed. This changes more or less rapidly through purple and crimson to a bright cherry-red tint, which is somewhat persistent." From this it was evident that ferric iron must be absent and probable that the vanadium must be in the pentavalent state. We confirmed the latter by trials of concentrated sulphuric-acid solutions of V_2O_5 , which gave no color with strychnine. This is an important point, for we found that strong sulphuric-acid solutions of vanadium pentoxide are very prone to go over to the quadrivalent state, when of course they develop no color with strychnine. With sulphuric-acid solutions of the phosphomolybdate precipitate containing vanadium, it is easy to follow this change by the change of color in the solution. Initially there is a straw or orange color,¹³ apparently due to the presence of acid vanadates or polyacids,¹⁴ which is probably closely proportional to the amount of vanadium present, but after a few minutes evaporation to strong sulphur trioxide fumes, and with low vanadium content, the solution becomes either colorless or a pale blue. We observed the same phenomenon with concentrated-sulphuric acid solutions of vanadium pentoxide. At first the reduction was thought to be due to organic matter present in the sulphuric acid, but further experiments with larger amounts of vanadium showed too much reduction to be accounted for in this way. For instance, in one experiment 8 milligrams of vanadium as pentoxide dissolved in 15 to 20 cc of sulphuric acid was fumed in a carefully covered flask for four or five hours, at the end of which time reduction was practically complete.

We found that Prandtl¹⁵ had already investigated this matter and concluded that under these conditions there is a dissociation of the vanadium pentoxide in analogy to the behavior of chromic anhydride dissolved in concentrated sulphuric acid. The behavior

¹² Commercial Organic Analysis, 2d ed., 3 pt., II, p. 368.

¹³ Some work has been done here toward making this color the basis of a colorimetric method for vanadium.

¹⁴ Gmelin-Kraut, Handb. d. Anorg. Ch., 7th Auf., III, 2, p. 89.

¹⁵ Gmelin-Kraut, Loc. cit., p. 87.

was the opposite of what we had expected, after having read the work of Koppel and Behrendt,¹⁶ who found the reverse action taking place. Possibly there is an equilibrium between the two sets of reactions. This complication is very troublesome when attempting to prepare the sulphuric-acid solution of the vanadium-bearing phosphomolybdate for colorimetric estimation by strychnine. As stated above, with small amounts of vanadium (for which we had expected the colorimetric method to be very useful), the reduction or dissociation takes place completely in a few minutes after the precipitate is dissolved in sulphuric acid. Such a solution treated at once with strychnine either gives no color, or a much less intense color than corresponds to the actual amount of vanadium present. On the other hand, if the attempt is made to reoxidize the vanadium to the pentavalent stage, this must be accomplished under difficult conditions, for no excess of the oxidizer must be left in the solution (inasmuch as this would give a color with the strychnine), nor must the solution be heated unduly long in attempting, for instance, to destroy or drive off the excess of oxidizer, for as soon as the excess disappears the vanadium goes quickly to the quadrivalent stage. Thus, while it was easy to oxidize the vanadium with a minute quantity of nitric acid, we could never be sure that the excess had been driven off and at the same time no vanadium had been reduced. We attempted to find an oxidizing agent that would oxidize the vanadium without affecting the strychnine and found that bismuthate would do so under very special sets of conditions, but there were complications attending its use, such as clouding of solutions in the colorimeter, occasional unexplained development of color in blanks, etc., that led us to abandon its use altogether. Besides the uncertainties and complications occasioned by solution in concentrated sulphuric acid already mentioned, which necessitate oxidation with reagents liable to cause high results if used (or low ones if not used), and those arising from the presence of iron with the phosphomolybdate, necessitating reprecipitation, there is also the possible accidental introduction of organic matter at various stages where reduction of vanadium might occur, and the troublesome manipulation of

¹⁶ Zs. Anorg. Chem., 35, p. 156; 1903.

concentrated sulphuric acid in the colorimeter. The colorimetric method of determining vanadium in the precipitate at first appealed to us because of its apparent simplicity and wide range of application, but the results of an extended series of determinations lead us, for the present at least, to abandon these views.

6. REDUCTION OF THE VANADIUM BY HYDROGEN PEROXIDE

(a) GENERAL

In attempting to find a suitable oxidizer for preparing the vanadium solutions for colorimetric determination we tried hydrogen peroxide, and were thus led to the discovery of the reaction which is made the basis of the method we have finally adopted for determining vanadium in the phosphomolybdate precipitates. Much to our surprise, the peroxide, used in concentrated sulphuric acid solutions, acted as a reducing instead of an oxidizing agent, so that by its use we were able to easily reduce the vanadium quantitatively to the tetravalent stage. Moreover, we found by careful tests that the associated iron and molybdenum were never affected. We found that solid peroxides could be used, but hydrogen peroxide is to be preferred, in general. The details of the reaction will be given fully in another paper, and only stated here in so far as they apply to the method of analysis. To carry out the reduction all that is necessary is to dissolve the phosphomolybdate-vanadium precipitate in concentrated sulphuric acid (filtration having been made on asbestos), add a few drops of nitric acid, fume strongly for two or three minutes, remove from the hot plate, allow to cool, and add hydrogen peroxide in very small quantities, with vigorous shaking after each addition, until the solution takes on a deep brown color (due to action on the molybdate); this always disappears on heating, and is followed by the clear green or blue color (depending on the ratio of V to Mo) of vanadyl vanadium. The flask is replaced on the hot plate and the solution fumed for a few minutes, after which it is cooled, diluted, and titrated against permanganate. The whole operation is extremely simple, the end point very good, and as our data show, the results are very accurate.

(b) THE METHOD

For Steels Containing Vanadium, Chromium, Nickel, Titanium, Manganese, Molybdenum, Singly, or in Combination.—Dissolve an amount of drillings estimated to contain 2 to 10 mg of vanadium in nitric acid (sp. gr. 1.135), boil till free from fumes, oxidize with permanganate solution, dissolve the separated manganese peroxide in sodium sulphite solution, and boil till free from fumes. In other words, prepare the solution exactly as for a phosphorus determination, examining any residue for vanadium. Nearly neutralize with ammonium hydroxide (0.96) and add an amount of sodium phosphate solution containing at least 10 times as much phosphorus as there is vanadium present. Bring the solution to boiling, remove from the plate and add at once the usual necessary excess of the molybdate reagent to precipitate the amount of phosphoric acid added. Agitate for a minute or so, when it will be found that the precipitate settles rapidly. Filter the supernatant liquid by suction through an asbestos filter, and wash three times by decantation with hot acid ammonium sulphate solution, pouring the washing liquid through the filter. The last wash solution should be decanted off as completely as possible from the precipitate in the flask and the filter should be sucked dry. The rubber stopper carrying the filter is now fitted to a small, dry, bottle and hot concentrated sulphuric acid is poured on the filter to dissolve the small amount of precipitate thereon. This dissolves quickly, and the solution is drawn through by suction into the bottle. The contents of the bottle are transferred to the flask in which precipitation was made, and the bottle is washed once with concentrated sulphuric acid, the washings being added to the flask. For every 10 mg of phosphorus present a final volume of 5 to 8 cc of concentrated sulphuric acid is necessary. The contents of the flask are heated until solution takes place, a few drops of nitric acid (1:25) are added, the heating is continued, and when fumes are coming off strongly, the flask is removed from the plate and the vanadium reduced by successive small additions of hydrogen peroxide, as above described. Replace on the hot plate, fume for four or five minutes, cover the flask, cool, dilute

so as to secure an acidity of one part to five by volume, and titrate at a temperature of 70° to 80° C against 0.01 N permanganate. The conditions as to acidity and temperature must be closely observed in order to secure a satisfactory end point.

For Steels of the Above Classes Containing Tungsten.—The only change necessary is to dissolve in aqua regia, dilute with hot water, filter off the tungstic acid, nearly neutralize with ammonium hydroxide, and add 10 g solid ammonium nitrate for every 100 cc of the final volume¹⁷ before precipitating as above described. If desired, the tungstic acid on the filter may be dissolved in a small amount of sodium hydroxide solution (free from vanadium), acidified with nitric acid, and tested for vanadium by hydrogen peroxide. We have not found vanadium here and accordingly make no provision for its determination.

(C) SOLUTIONS NECESSARY

Nitric Acid of Sp. Gr. 1.135.—Use 20–25 cc for each gram of drillings to be dissolved.

Potassium Permanganate, for Oxidations, 15 grams per liter.

Sodium Sulphite, 50 grams per liter. A solution of sulphurous acid may be substituted.

Sodium Phosphate, 124 grams $\text{Na}_2\text{HPO}_4 \cdot 12 \text{ H}_2\text{O}$ per liter. One cubic centimeter contains approximately 10 mg of phosphorous and will precipitate 1 mg of vanadium. The solution may be standardized by evaporating a definite volume to dryness, igniting the residue, and weighing the $\text{Na}_4\text{P}_2\text{O}_7$ so formed.¹⁸

Molybdate Reagent.—Made up according to the usual formulas, 1 cc will contain 0.05 to 0.06 g MoO_3 . For every mg of phosphorus to be precipitated use at least 2 cc of molybdate reagent. This ratio is used, however, only when precipitating large amounts of phosphorus. When precipitating small quantities of phosphorus 50 cc of molybdate solution is the minimum volume used.

Acid Ammonium Sulphate.—To 1000 cc of water add 15 cc of ammonium hydroxide (0.90) and 25 cc of sulphuric acid (1.84).¹⁹ Use at a temperature of 80° C.

¹⁷ Bureau of Chemistry Bull. No. 107 (revised), p. 3.

¹⁸ Baxter: Am. Chem. J., 28, p. 301; 1902.

¹⁹ Blair: The Chemical Analysis of Iron, 7th ed., p. 97.

Potassium Permanganate, 0.01N.—Standardize against sodium oxalate,²⁰ or, empirically, against a steel in which the vanadium has been accurately determined by other methods.

Peroxide.—Hydrogen peroxide, 3 per cent; we have made our reagent with "Perhydrol." "Dioxogen" also proved satisfactory.

Table II shows a few of the very large number (in all nearly 400) of determinations made by us to be sure that the method is reliable. Nos. 16 and 17 of the same table are of interest as showing the delicacy of the method. As a matter of fact, the vanadium can just as easily be concentrated from 50 or even 100 g of steel or iron, so that excessively small percentages can be detected and determined with ease. Nos. 19, 20, 21, and 22 of the same table show the application to other materials, the results on the titaniferous magnetite being of special interest.

If the expected content of vanadium in a sample is not known accurately enough for adding the necessary excess of phosphoric acid, two or more precipitations may be necessary.

We have found the arrangement shown in Fig. 1 useful for handling the concentrated sulphuric acid; it is much more convenient to use than a reagent bottle. It stands on a large sheet of glass. Also, the funnel with glass stopper (Fig. 2) is useful but not necessary. It is made by sealing a carbon filter to the inlet tube of a thick-walled glass wash bottle, the latter being used as a suction filter flask. If rubber stoppers are used, they should be good sound ones, so that pieces of rubber can not drop into the concentrated sulphuric acid solutions.

²⁰ Bureau Standards Circular No. 26, 2d ed., p. 10.

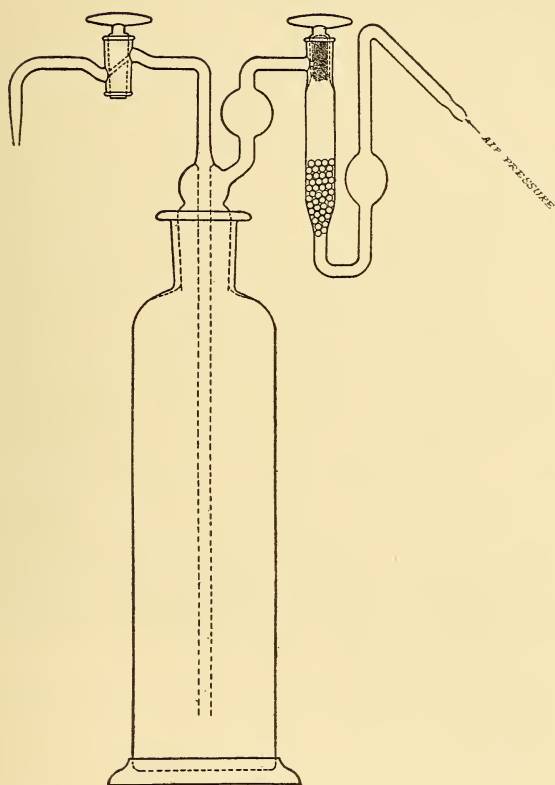


Fig. 1

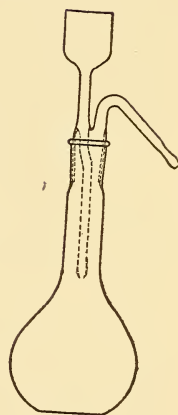


Fig. 2

TABLE II
Results Obtained by the Peroxide Reduction Method ²¹

No.	Amount	Cr present	P added	V present	V found	V ₂ O ₃ found
	g	mg	mg	mg	mg	Per cent
²² 1	1	45	12	1.11	1.17
2	1	180	20	1.92	1.91
3	1	135	35	3.19	3.26
4	1	90	45	4.52	4.60
5	1	45	60	6.38	6.49
6	1	225	100	10.64	10.73
²³ 7	1	50	10	1.02	1.16
8	1	100	25	2.54	2.58
9	1	150	40	4.06	4.15
10	1	200	50	5.08	5.07
11	1	250	60	6.08	6.18
12	1	50	80	8.13	8.40
13	1	100	90	9.12	9.42
14	1	150	100	10.15	10.22
²⁴ 15	5	19	0.995
16	20	20	1.00	1.02
17	20	19	1.11	1.24
²⁵ 18	1	25	2.66	2.75
²⁶ 19	2	19	1.07	0.078
²⁷ 20	10	39	3.41	0.05
²⁸ 21	10	19	0.66	0.01
²⁹ 22	10	19	0.81	0.012

²¹ Except as otherwise indicated, the solutions used for these determinations were made by adding chromium and vanadium to the nitric-acid solution of a vanadium and chromium-free steel, in the proportions indicated in the table. The vanadium was added from an ammonium vanadate solution, which was standardized by reducing with sulphur dioxide and titrating against permanganate; the chromium was added from a chrome-alum solution, the chromium content being calculated from the amount of salt weighed out.

²² Nos. 1 to 6, and 15 to 22, inclusive, reduced with magnesium peroxide.

²³ Nos. 7 to 14, inclusive, reduced with hydrogen peroxide.

²⁴ No. 15, Bureau of Standards. Chrome-Tungsten Steel Standard (in preparation) V found=0.02 per cent (not determined by any other method).

²⁵ No. 18 contained 23 mg of titanium as titanium sulphate.

²⁶ No. 19, Bureau of Standards Magnetite Ore, No. 29. B. S. Chemist's value 0.075% V₂O₃.

²⁷ No. 20, Bureau of Standards Manganese Ore, No. 25.

²⁸ No. 21, Bureau of Standards Sibley Ore, No. 27.

²⁹ No. 22, Bureau of Standards Crescent Ore, No. 26.

The largest amount of vanadium determined in Table II (10.64 mg, or about 1 per cent on a 1-g sample) gives about as large a volume of precipitate as it is convenient to handle. We have precipitated and determined accurately as much as 27 mg of vanadium, using the 10 to 1 ratio of phosphorus, but the manipulation in such cases becomes inconvenient. This is about the only serious limitation placed on the method, making it necessary when dealing with large amounts of vanadium to precipitate from an aliquot corre-

sponding to a relatively small sample. For steels, alloys, ores, rocks, etc., containing from traces up to 5 or 6 per cent of vanadium, the method, we believe, can be used wherever phosphorus can be precipitated as phosphomolybdate from solutions of these materials.

7. NOTES AND PRECAUTIONS

The presence of vanadium in the phosphomolybdate precipitate is shown by the yellow to orange color of the cold concentrated sulphuric acid solution of the precipitate, 0.05 mg vanadium showing a perceptible color in a volume of 25 cc.

In carrying out the peroxide reductions it is necessary to use a flask instead of an open dish or beaker. If the latter is used, there is reduction of the molybdenum where the strong acid solution "creeps" up along the sides of the vessel, the reduction showing by the development of an intense blue coloration.

If after the addition of peroxide and subsequent heating, the vanadium is not reduced, it is probably due to traces of nitric acid in the solution, which may be removed by further fuming; the treatment with peroxide should then be repeated. In this connection, we may note that nitrous fumes readily oxidize tetravalent vanadium, and hence the reductions should be carried out in an atmosphere free from such fumes.

After the reduction it is advisable to cover the flask with a watch glass while the solution is cooling, in order to prevent accidental introduction of organic matter.

If the final titration is carried out in acid of greater concentration than one to two by volume, the end point is rendered uncertain, because of the deep yellow color which the pentavalent vanadium, formed during the titration, gives with strong sulphuric acid. We recommend a dilution of one to five, in which the end point is very sharp.

The time required for making a determination is worthy of note. Working with vanadium steel, the sample was weighed out, dissolved, and precipitated in 10 minutes, the precipitate washed and dissolved in sulphuric acid in 9 minutes more, while the reduction and titration required a further 12 minutes, giving the completed determination in approximately one-half hour. By operating on

a large number of samples at one time, the determination can be made as rapid as, if not more rapid, than that of phosphorus in steels. We have frequently completed 20 determinations in less than 7 hours, even while giving much attention to uncompleted details. With these worked out, the method should allow the completion of twice as many determinations in a day.

Manganese ores are readily decomposed with hydrogen peroxide in the presence of nitric acid. This solution is very well adapted for the determination of vanadium. The insoluble should also be tested for vanadium.

When precipitating vanadium from a solution containing hydrochloric acid and, in general, when the volume of the solution is very great, we recommend the addition of 10 g of solid ammonium nitrate for every 100 cc of solution.

8. SUMMARY

1. It was found that vanadic acid may be quantitatively precipitated by ammonium phosphomolybdate.

2. The vanadium-bearing phosphomolybdate shows different solubility relations compared with the normal phosphomolybdate with respect to the usual washing solutions used in determining phosphorus.

3. Conditions are given for quantitatively precipitating vanadic acid when in solution alone, or accompanied by a variety of other elements, by means of ammonium phosphomolybdate.

4. In order to determine quantitatively the vanadic acid so precipitated, (a) the possibility of freeing it from accompanying molybdic acid was investigated; (b) conditions for reducing it without reducing the associated molybdic acid were developed; and (c) a method for reducing it by hydrogen (and other) peroxides and titrating it against permanganate was elaborated.

5. Method (c) was applied to a variety of steels, to iron ores, manganese ores, and to synthetic mixtures, in all of which the vanadium was determined with great accuracy.

WASHINGTON, October 26, 1911.



